

STATE OF CALIFORNIA
AIR RESOURCES BOARD

AIR MONITORING QUALITY ASSURANCE

VOLUME V

AUDIT PROCEDURES
FOR
AIR QUALITY MONITORING

APPENDIX W

PERFORMANCE AUDIT PROCEDURES
FOR
THROUGH-THE-PROBE NON-METHANE HYDROCARBON (NMOC) AUDITS

MONITORING AND LABORATORY DIVISION

MAY 2002

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PERFORMANCE AUDIT PROCEDURES
FOR
THROUGH-THE-PROBE NON-METHANE HYDROCARBON (NMOC) AUDITS

MONITORING AND LABORATORY DIVISION

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W.1.0 INTRODUCTION

W.1.0.1 GENERAL INFORMATION

Non-methane hydrocarbon (NMOC to distinguish it from the instrumental method) through-the-probe audits are conducted annually at each site by the Quality Assurance Section (QAS). A sample container is filled with known (assigned) concentrations of audit gases during a three-hour period. The sampler is run, wherever possible, in conditions duplicating a routine ambient run. The analytical laboratory is not notified of the audit until after it analyzes the sample. The QAS then requests the analytical results and calculates the percent difference of the sample for various NMOC compounds:

$$\text{Percent Difference} = \left[\frac{\text{Measured Concentration} - \text{Assigned Concentration}}{\text{Assigned Concentration}} \right] \times 100$$

The purpose of a through-the-probe audit is to assess the accuracy of the total measurement system, including: errors inherent in contamination in transport, effects of sample pump and probe, and laboratory error.

W.1.0.2 FIELD NOTIFICATION

The QAS arranges the audit with the station operator 10 days to 2 weeks before the audit date. The station operator is requested not to inform the laboratory that the sample is an audit sample. Special or differentiating markings are not put on the canister to identify it as an audit sample.

W.1.0.3 CAUTIONS

Avoiding contamination is critical since the organic compounds being generated by the dilution system are present in low concentrations, generally in the 1.0 to 15.0 ppb range. Whenever possible, silica-lined stainless steel (SS) tubing will be used to introduce the audit sample to the probe inlet. All lines and fittings in the dilution system must be cleaned periodically and capped when not in use. Further, during each audit, there must be a positive pressure at the manifold “T” (1 liter/per minute minimum excess bypass flow) where the dilution system output connects to the sample probe.

NOTE: The cleaning procedure is performed every 120 days. All lines in the dilution system are flushed with a Liqui-NO_xTm solution followed by distilled water and air dried. All SS fittings are soaked in a Liqui-NO_xTm solution and cleaned ultrasonically.

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PERFORMANCE AUDIT PROCEDURES
FOR
THROUGH-THE-PROBE NON-METHANE HYDROCARBON (NMOC) AUDITS

MONITORING AND LABORATORY DIVISION

MAY 2002

W.2.0 AUDIT PROCEDURES

W.2.0.1 APPARATUS

1. Dilution Unit (EnviroNics 2014) with MFCs/MFMs
2. NMOC Gas Cylinder with SS Regulator
3. Humidification apparatus
4. Nano-pure water
5. Vol-o-Flow gauge 0 - 15 LPM
6. 1/4" silica-lined stainless steel tubing
7. RH meter

W.2.0.2 DETERMINATION OF DILUTION RATIO

The dilution ratio to be used for the audit is defined as follows:

$$\text{Dilution Ratio} = \frac{\text{Gas Flow}}{\text{Air Flow} + \text{Gas Flow}}$$

This ratio is calculated, approximately, prior to the audit, and depends on several factors, including assigned cylinder concentrations, required minimum air flow, gas flow (cannot exceed 1000 cubic centimeters per minute (CCPM)) and the requirement to generate hydrocarbon concentrations greater than the minimum detectable limit to permit quantitative lab analyses. In general, the desired concentration of hydrocarbons in the audit gas stream is in the range of 1.0 to 15.0 ppb. Once the desired concentration is chosen, the dilution ratio and the required flow settings are determined according to the following example for ethane (C₂H₆).

1. Desired gas concentration (assigned value): 11.0 ppbC C₂H₆

Assigned NIST Cylinder Value: 1100.0 ppbC C₂H₆

$$\text{Dilution Ratio, calculated} = \frac{11.0 \text{ ppbC}}{1100.0 \text{ ppbC}} = \frac{1}{100}$$

NOTE: The concentration of ethane is ppbC (parts per billion carbon). Typically, the concentrations of the remaining compounds in the cylinder are in the same range as ethane, so the calculated dilution ratio permits quantitative analyses of all compounds.

2. If we find the probe flow measures 3.5 LPM (Ref: Sect. W.2.0.3, Step 4) and we require a manifold bypass flow of 1.0 LPM,

$$\begin{aligned}\text{Required Air Flow} &= 3.5 \text{ LPM} + 1.0 \text{ LPM} \\ &= 4.5 \text{ LPM (True Flow)} \\ &= 4500 \text{ ccpm}\end{aligned}$$

3. Substitute and solve for Gas Flow,

$$\text{Dilution Ratio} = \frac{\text{Gas Flow}}{\text{Air Flow} + \text{Gas Flow}}$$

$$\frac{1}{100} = \frac{\text{Gas Flow}}{4.5 + \text{Gas Flow}}$$

$$\begin{aligned}\text{Gas Flow} &= 0.0455 \text{ LPM} \\ &= 45.5 \text{ CCPM (True Flow)}\end{aligned}$$

4. Using the Environics correction equations from the lab's latest calibration report (certified every quarter), calculate the required air and gas flow rates for the Environics. The front display and key pad will be used to set the flow rates for the desired mass flow controllers. The following results are from a typical calibration:

$$\begin{aligned}\text{Gas: Display} &= 1.0947 * \text{True Flow} + 0.3180 \\ &= 1.0947 * 45.5 + 0.3180 \\ &= \underline{50.1 \text{ CCPM}}\end{aligned}$$

$$\begin{aligned}\text{Air: Display} &= 0.0011 * \text{True Flow} + 0.0098 \\ &= 0.0011 * 4500 + 0.0098 \\ &= 4.96 \text{ LPM} \\ &= \underline{4960 \text{ CCPM}}\end{aligned}$$

W.2.0.3 STATION PREPARATION

1. Perform leak check #1 (see Section W.2.0.5).
2. Ensure the sample canister valve is closed after leak check #1 and disconnect the line from the canister.
3. Switch on the sampler (timer override on "I", the manual ON position). Connect a Vol-o-Flow gauge (vacuum side) to the end of the probe line to determine the sampler flow demand. Record the vacuum reading on the NMOC/PAMS Datasheet.

NOTE: There may be a 30-minute delay if the sampler requires a warm-up period.

4. Perform leak check #2 (see Section W.2.0.5).

NOTE: Both leak checks should be completed before any gas is introduced into the system via the Environics.

5. Attach a stainless steel ¼ inch “T” to the end of the station’s probe using a stainless steel nut and ferrule. Connect the leg that would flow “straight through” to a ¼” Teflon[®] line, via a stainless steel nut and ferrule, to serve as a bypass line. Connect the “T” portion (90 degree angle to the other two) of the stainless steel “T” to a ¼” stainless steel audit probe line and connect the other end to the output of the Environics 2014. The bypass line will be used to measure bypass flow rates and humidity using the Vol-o-Flow and RH meter respectively

NOTE: If it is not possible to connect to the stations sample probe inlet, the connection can be made at the input of the sampler. The bypass “T” is still used but the bypass line must be vented outside of the building.

6. Turn on the portable API 701 zero air generator. Set the output pressure to 35-45 PSIG, if necessary (Figure W.2.0.4).
7. Connect a Vol-o-Flow gauge (vacuum side) to the end of the probe line to determine the sampler flow demand. Record the flow rate on the NMOC sampler audit worksheet (Figure W.2.0.3).

W.2.0.4 DILUTION SYSTEM PREPARATION

(Refer to Figure W.2.0.4 for diagram of audit setup.)

1. Connect the output port of the API to port #1 of the Environics. Ensure fittings are snug, but do not overtighten as the threads on the ports are easily stripped or damaged.
2. Connect a ¼” Teflon[®] line to the vent port of the Environics and ensure the end of the line is outside of the building. Failure to do so will allow various gases to accumulate inside of the building.
3. Install the humidifier flask and tubing (See Figure W.2.0.5). Ensure the flask stopcock is closed and fill with nano-pure water. Place the end of the drain line in a drain cup and open the stopcock on the flask. Water will flow through the humidifier rail and tubing. Once all air bubbles have been flushed out of the rail and tubing, shut off or disconnect the quick

disconnect (depending upon which tubing used) on the tube connected to the bottom of the humidification rail. Refill flask. Ensure that stopcock on flask remains open for the duration of the audit so water can flow into the humidifier rail.

4. Turn on the API and Environics. If the old configuration API is used (no flow restriction on output), NEVER switch on the API without having installed the API output to port #1 of the Environics. Failure to do so will cause water damage and contamination of the API and invalidate all audit results until it is re-certified clean by the laboratory.
5. Once the API has pressurized and stabilized, enter into flow mode on the Environics and set port #1 to the air flow you determined in your dilution ratio earlier (usually 4000 ccm). This is the beginning of the 1-hour air purge. Record your start time and end times on the audit worksheet.
6. Connect a stainless steel regulator to the audit gas cylinder. Purge the regulator three times by opening and closing the regulator briefly. Connect a 1/4" stainless steel line from the regulator to port #3 of the Environics. Pressurize the gas line by setting your regulator to 25 psi. Once pressurized, shut off the regulator by turning it counter-clockwise until it stops. Note the regulator pressure. In 5 minutes, check pressure on regulator again. If it is still at the set pressure (roughly 25 psi), the line is free of leaks. If the pressure has fallen, re-check line for cracks and fittings for leaks. Replace the line if necessary and recheck

CAUTION: Do not proceed with the audit until you can ensure that the gas line is free of leaks. Failure to do so can drain the cylinder over the course of the audit and contaminate the building with toxic audit gases.

7. After the 1-hour zero air purge, open the valve on the gas cylinder and adjust the output pressure to 25 PSIG. Set Environics port #3 to desired gas flow (usually 40 ccm). **Allow 30 minutes of diluted gas purge of the whole system.**

CAUTION: Be watchful of the regulator pressure, it may drop, and adjustments may be needed for the first few minutes.

8. After the 30-minute gas purge, ensure that the sampler's sample line is securely connected to the canister. Open the canister's valve and verify that the sampler has begun sampling (the counter will be counting).
9. Verify the bypass flow rate at the "T" using a rotameter capable of reading 0-2 liters per minute. Also, measure the %RH at the bypass in a closed container. The %RH should be in the range of 50% - 80%.

10. Record the target air and gas flow rates in the appropriate mass flow controller boxes on the NMOC sampler audit worksheet. Record all pertinent data on the data sheet, such as: initial turn on times, sampler flow, sampler back pressure setting, manifold bypass flow, results of leak checks, beginning humidity reading, etc.

W.2.0.5 LEAK CHECKS

Check the sampler and probe and canister lines for leaks as follows:

1. Leak check #1-With the sampler off, check for leaks in the sampler inlet solenoid and canister inlet fitting. Connect an evacuated canister to the sample output line and open the canister inlet valve by turning the knurled knob counterclockwise. Ensure the sampler is on the position where the canister was connected if multiple cans may be sampled. After the sampler gauge shows a vacuum reading, close the canister valve and record the vacuum reading. After 30-minutes, take another reading. If there is any change, there is a leak in the system. Tighten fittings and repeat this step. If leak persists, notify site operator and determine if leak is repairable. If not, do not proceed with the audit. Issue an Air Quality Data Action Request (AQDA).

CAUTION: If the canister gauge reads less than -26 "Hg", do not proceed with the audit unless another canister is available.

2. Leak Check #2-Disconnect the canister from the sample output line and with the sampler running, check the probe line for leaks. Turn the sampler on and verify there is a flow on the front gauge. Temporarily disconnect the audit probe line and cap the probe inlet at the roof. Place a Vol-o-Flow gauge on the exhaust by-pass port at the rear of the sampler. If there is no leak, the Vol-o-Flow gauge reading should drop to zero. The indicated sample flow at the front gauge of the instrument should also drop to zero. If flow reaches zero on both gauges, leak check #2 has passed. Record this on your worksheet. Reconnect the audit probe line and the audit canister.

If the flow does not reach zero, loosen and retighten probe nut and check all fittings to ensure they are snug. Repeat procedure. If you are unable to obtain a zero reading on both the sampler gauge and the Vol-o-Flow, there is a leak in the system. Notify the site operator and try to determine where the leak is. Disconnect the sampler's inlet line at the back of the instrument and cap the inlet port. The indicated flow should drop to zero. If the flow does not drop to zero, this indicates there is a leak within the sampler. If the flow drops to zero, this indicates a leak in the probe line. Regardless of where the leak is, Leak check #2 will be a failure. Record this on the audit worksheet and discontinue the audit. Issue an AQDA.

W.2.0.6 END RUN PROCEDURE

1. At the end of the three-hour audit period, record the final data readings on the NMOC sampler audit worksheet: canister end pressure, cylinder end pressure, audit end time, %RH end, and pertinent site information (probe length, probe material, siting information, etc.). Also complete the NMOC/PAMS Datasheet.
2. Visually check that the canister has filled to 8-16 psi. Close the inlet valve on the canister and disconnect the sampler output line.
3. Dial in zero for Port 3 on the Environics to turn off supply of audit gas.
4. Close the main valve on the audit cylinder and remove the SS regulator.
4. After five minutes of clean air purge, disconnect the sample probe line.
5. Switch off the sampler.
6. Switch off power to the API 701 and the Environics.
7. Disassemble all audit lines and cap each to prevent contamination.
8. Disassemble the humidification system.
9. Re-install the sample probe, as necessary, in its original location.
10. Return all station lines, timers, etc., to their original configuration.

QA AUDIT WORKSHEET NMOC SAMPLER

Site Name: _____ Site #: _____ Date: _____
Address: _____ Agency: _____
Technician: _____ Auditors: _____
Quarter: 1[] 2[] 3[] 4[] Standards Version: _____ Year: _____

SAMPLER INFORMATION

Sampler Make/Model: _____ Multicanister Cal. Date: _____
Sampler ID#: _____ Canister ID#: _____
Sampler Cal. Date: _____ Canister Start Pressure: _____
Multicanister Sam. ID#: _____ Canister End Pressure: _____

Sampler By-Pass Total
Flow Rate _____ Flow Rate _____ Flow Rate _____

AUDIT INFORMATION

Dilution Unit	
Make:	
Model:	
ID#:	

Pure Air Source	
Make:	
Model:	
ID#:	

Audit Cylinder		
ID#:		
Pressure	Initial	Final
(PSI)		

Dilution Unit Flow Rates	
MFC #1	CCM
MFC #2	CCM
MFC #3	CCM

Purge Times		
	Start	Stop
Zero Air		
Sample Air		

Audit Parameters		
	Start	Stop
Time		
% RH		

Comments: _____

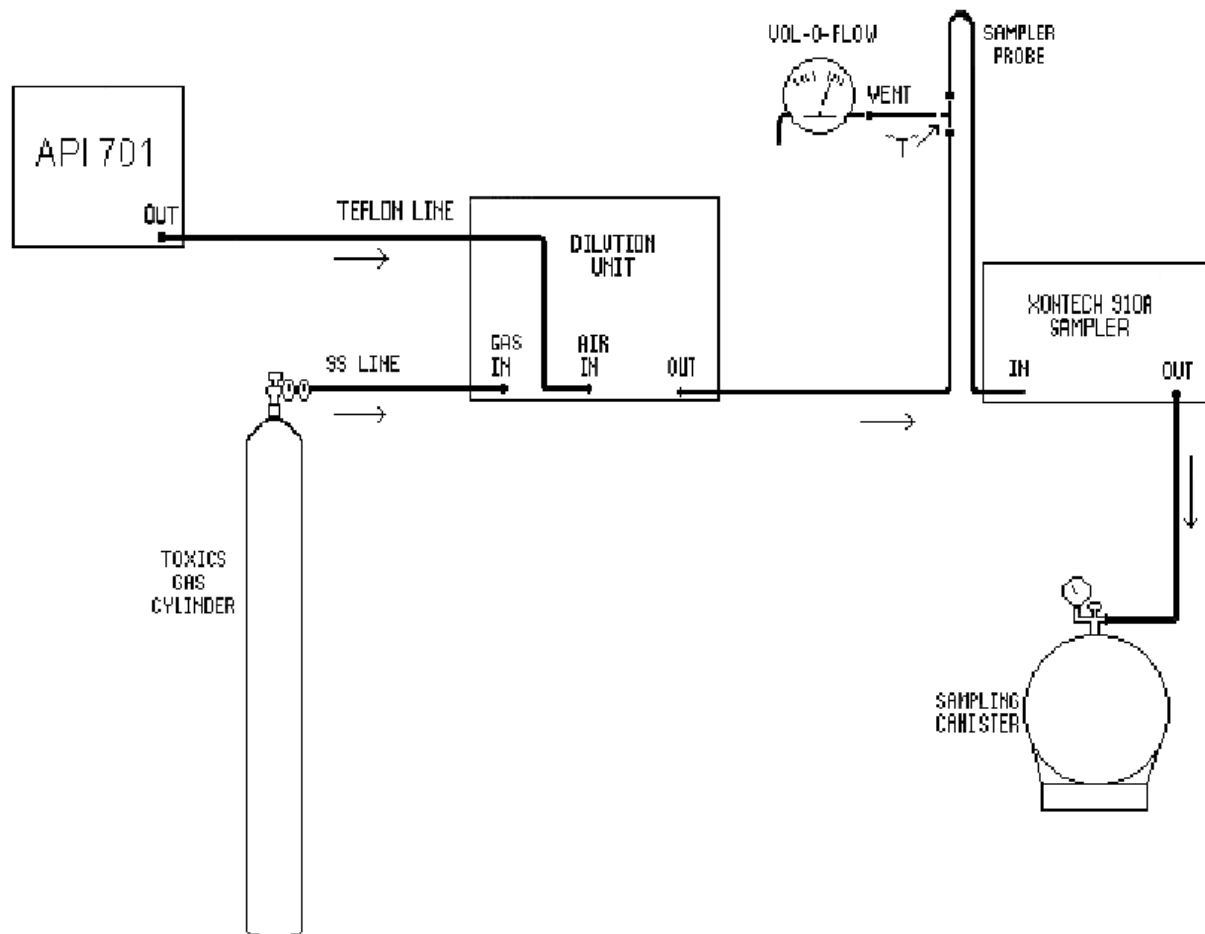


Figure W.2.0.4
Diagram of Audit Setup

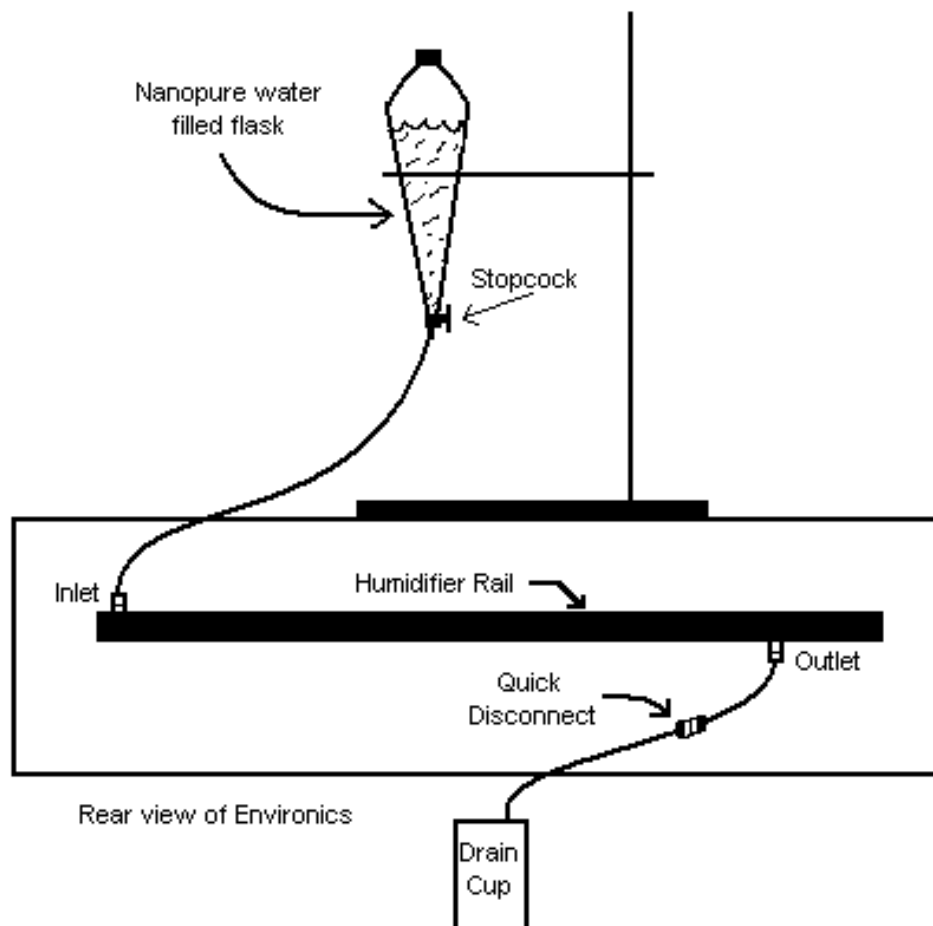


Figure W.2.0.5
Diagram of Humidification Setup

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FOR
THROUGH-THE-PROBE NON-METHANE HYDROCARBON (NMOC) AUDITS

MONITORING AND LABORATORY DIVISION

MAY 1998

W.3.0 POST AUDIT CALCULATIONS

W.3.0.1 CALCULATION OF PERCENT DIFFERENC

After the analytical laboratory analyzes the contents of the sample container, obtain the lab results (measured concentrations). Calculate the percent difference for each compound in the audit sample using the following equations:

Assigned Value = Dilution Ratio x Assigned Cylinder Value.

$$\text{Percent Difference} = \left[\frac{\text{Measured Concentration} - \text{Assigned Cylinder Value}}{\text{Assigned Cylinder Value}} \right] \times 100$$

The results are presented in a report as shown in Figure W.3.0.1.

Quality Assurance Thru-the-Probe NMHC Audit Technical Appendix

Instrument/AIRS Information								
ARB Number	20211	AIRS Number	060390004					
Audit Date	02/01/2002	Laboratory	AAC Can 5014(T1)					
Audit Concentration Calculations								
Diluted Conc. (ppbC) = NIST Conc. * Dilution Ratio								
Percent Difference = (Average - Diluted Conc.)*100/Diluted Conc.								
Audit Concentration versus Laboratory Response Data								
Compound	NIST Conc. (ppbC)	Dilution Ratio	Diluted Conc. (ppbC)	Run 1 (ppbC)	Run 2 (ppbC)	Run 3 (ppbC)	Average (ppbC)	Percent Difference
Ethane	1134	1/101	11.2	11.8	12.2	12.5	12.2	8.9%
Ethene	988	1/101	9.8	10.7	11.0	10.7	10.8	10.2%
Propane	1119	1/101	11.1	12.9	12.2	12.8	12.6	13.5%
2-Methylpropane	852	1/101	8.4	8.5	8.8	9.1	8.8	4.8%
1-Butene	656	1/101	6.5	7.0	7.5	7.0	7.2	10.8%
Pentane	790	1/101	7.8	7.7	8.5	7.2	7.8	0.0%
1-Pentene	900	1/101	8.9	8.7	8.9	8.8	8.8	-1.1%
2-Methylpentane	1122	1/101	11.1	10.9	11.4	11.6	11.3	1.8%
Hexane	524	1/101	5.2	6.4	6.0	6.9	6.4	23.1%
Benzene	936	1/101	9.3	10.9	10.9	10.2	10.7	15.1%
3-Methylhexane	344	1/101	3.4	3.7	3.5	3.7	3.6	5.9%
2,2,4-Trimethylpentane	794	1/101	7.9	8.2	8.4	8.1	8.2	3.8%
Methylcyclohexane	312	1/101	3.1	3.8	3.3	3.2	3.4	9.7%
Toluene	1519	1/101	15.0	15.4	15.2	15.8	15.5	3.3%
3-Methylheptane	752	1/101	7.4	7.6	7.6	7.5	7.6	2.7%
Octane	313	1/101	3.1	3.0	3.5	3.1	3.2	3.2%
Ethylbenzene	602	1/101	6.0	6.3	6.1	6.4	6.3	5.0%
m/p-Xylene	1344	1/101	13.3	13.4	13.7	13.9	13.7	3.0%
o-Xylene	547	1/101	5.4	5.4	5.5	5.8	5.6	3.7%
n-Propylbenzene	548	1/101	5.4	4.9	5.5	5.3	5.2	-3.7%
1,2,3-Trimethylbenzene	482	1/101	4.8	4.8	4.4	4.8	4.7	-2.1%
Decane	486	1/101	4.8	4.6	4.7	5.3	4.9	2.1%

California Air Resources Board
Monitoring and Laboratory Division
Quality Assurance Section

Figure W.3.0.1
NMOC Audit Report